



10.1117/2.1201103.003600

Detecting dangerous substances from their 2D spectra

Jacob Grun

Explosives, bacteria, and chemicals can be identified from their 2D resonance-Raman spectra, even when several substances are mixed together.

Identification of bacteria or chemicals with Raman spectroscopy is fast, noncontact, and does not require expendable supplies. These are all desirable characteristics for many applications. The technique uses a laser to illuminate the area that may contain the suspect substance. Some of the light is absorbed by the molecule of interest and then re-emitted at wavelengths that are slightly different from that of the

illuminating laser. The spectrum of this Raman-scattered light is unique to the substance's molecular-bond structure, constituting a signature that can be used for identification. But the fraction of laser light that is Raman scattered is very small, resulting in insufficient sensitivity for many practical situations. Furthermore, the illuminated region may contain many different substances, each scattering its own Raman spectrum. The sum can be quite complex and noisy, compromising specificity and the ability to identify the constituent species.

The sensitivity of Raman spectroscopy can be increased by illuminating the substance with specific laser-photon energies (or, equivalently, with particular laser wavelengths) that are resonant with the substance's vibrational and rotational states,

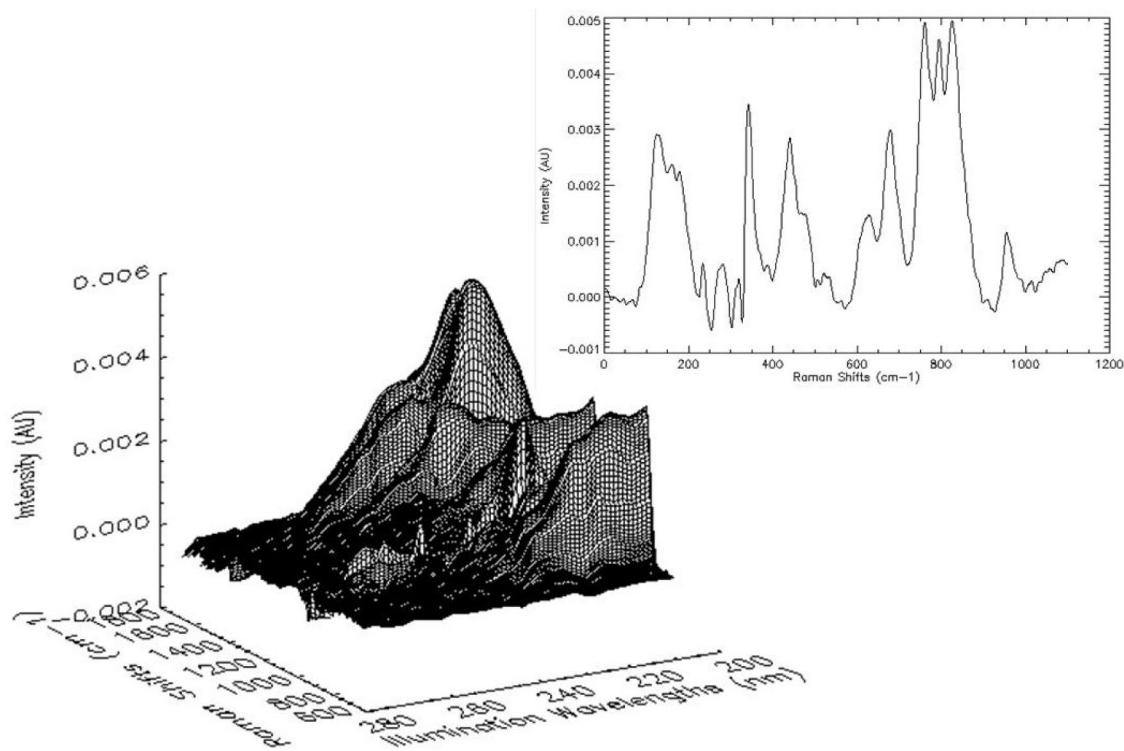


Figure 1. One- and two-dimensional resonance-Raman spectra of the explosive HMX. Spectra acquired by illumination with laser light of 261nm (top right) and light covering a range of wavelengths from 210 to 270nm (bottom left).

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Report Documentation Page			Form Approved OMB No. 0704-0188	
<p>Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p>				
1. REPORT DATE APR 2011	2. REPORT TYPE	3. DATES COVERED 00-00-2011 to 00-00-2011		
4. TITLE AND SUBTITLE Detecting Dangerous Substances From Their 2D Spectra			5a. CONTRACT NUMBER	
			5b. GRANT NUMBER	
			5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)			5d. PROJECT NUMBER	
			5e. TASK NUMBER	
			5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) US Naval Research Laboratory, Washington, DC, 20375			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSOR/MONITOR'S ACRONYM(S)	
			11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited				
13. SUPPLEMENTARY NOTES SPIE Newsroom: Optics and photonics technical articles, Apr 14, 2011				
14. ABSTRACT				
15. SUBJECT TERMS				
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON



a technique called resonance Raman.^{1,2} In these circumstances, the cross section for scattering is 100–100,000 times greater than for conventional Raman spectroscopy, and the number of photons emitted by an irradiated molecule is increased. In addition, the cross section near resonance is a function of the laser wavelength, so illuminating with a number of such wavelengths produces a series of spectra containing additional information that is useful for identification and improving the specificity. But this capability is hard to realize in practice. Current detectors use lasers that operate at a single wavelength, which is not necessarily in resonance with the bonds of the substance of interest, or that is resonant with bonds of one substance but not with those of another.

We are developing techniques to enable practical and automatic multiwavelength resonance-Raman identification.^{3–10} The swept-wavelength optical resonance-Raman detector (SWOrRD) sequentially illuminates a sample with a laser that is tunable from 210 to 2100nm in increments of up to 0.1nm and measures the spectrum of the scattered light with a two-stage tunable spectrometer. All components of the SWOrRD system are synchronized to the laser wavelength and operate automatically. It can switch from one wavelength to another in less than one second. SWOrRD's laser has a bandwidth of \sim 15cm⁻¹, average power from 10 to 400mW, and runs at 1KHz, resulting in low peak power. All these characteristics make it especially suitable for substance identification.

After acquisition, the raw spectra are processed with a semi-automated toolbox that corrects for system-response characteristics, smoothes noise, subtracts backgrounds, and performs the housekeeping tasks needed to produce device-independent spectral signatures. The individual resonance-Raman spectra acquired at each illumination wavelength are then assembled to form a single 2D signature, where the two independent dimensions represent laser-illumination wavelength and scattered-wave number. Various algorithms are applied that assume that the 2D spectrum of a mixture is a linear superposition of the 2D spectra of the mixture's components, and so use the signatures to identify the presence and amount of the substance or substances being sought. The signatures (see Figure 1) are also stored in a database where they are available to researchers.

In most practical situations, the substance of interest is not alone, but rather part of a mixture containing other chemicals, or present in the background. We have shown that 2D signatures can continue to identify the presence and amount of different substances in a mixture containing four explosives (HMX, RDX, pentaerythritol tetranitrate, and trinitrotoluene: TNT), when random noise levels caused identification based on 1D

spectra to fail.¹¹ We also demonstrated automatic identification of the presence and amounts of components in a mixture containing different amounts of water, methanol, ethylene glycol, ethanol, and acetonitrile. The spectral features of these chemicals overlap significantly, making automatic identification a challenge, yet they were readily identified with linear-mixture algorithms based on either methods adopted from the hyperspectral-imaging community^{11,12} or an iterative procedure based on the Pearson correlation coefficient.^{13,14}

In many parts of the world, the environment is already contaminated by traces of explosives that have been present for a long time but that do not automatically signal danger. This complicates identification of genuinely dangerous situations. We have shown that SWOrRD can distinguish fresh explosives from those that have been artificially aged by heating or exposure to UV light. SWOrRD can also differentiate between fresh TNT and its environmental-decomposition products.^{15,16}

Rapid identification of bacteria remains a major challenge. We have demonstrated that 2D resonance-Raman signatures can distinguish between bacteria, including species that are closely related as measured by their 16S ribosomal DNA sequences. For example, we can distinguish between *B. cereus* and *B. thuringiensis*, which are genetically similar to within 99.8%, and others that are genetically similar to within 97%.^{3,15}

We continue to develop both hardware and software to optimize the device's specificity, sensitivity, and robustness. To date, we have collected 2D signatures of approximately 140 different chemicals, explosives, bacteria, and mixtures, and continue to measure the signatures of species and backgrounds of potential interest. We hope to build a single detector that would be useful for a wide variety of chemical and biological applications, including scenarios related to health and national security.

This work is sponsored by the Office of Naval Research and by the Defense Threat Reduction Agency (DTRA: <http://www.dtra.mil>). DTRA was founded in 1998 to integrate and focus the capabilities of the Department of Defense that address the weapons of mass destruction (WMD) threat. The mission of the DTRA is to safeguard America and its allies from WMD threats (e.g., chemical, biological, radiological, nuclear, and high-yield explosives) by providing capabilities to reduce, eliminate, and counter the threat and mitigate its effects. Under DTRA, Department of Defense resources, expertise, and capabilities are combined to ensure the US remains ready and able to address present and future WMD threats.



Author Information

Jacob Grun

US Naval Research Laboratory
Washington, DC

Jacob Grun is chief of special projects in the Laser Plasma Branch of the Plasma Physics Division. He is the principal investigator of the SWoRD project. He is a fellow of the American Physical Society.

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